



Chemical reaction mechanisms between Y_2O_3 stabilized ZrO_2 and Gd doped CeO_2 with PH_3 in coal syngas



Gang Chen^{a,*}, Haruo Kishimoto^a, Katsuhiko Yamaji^a, Koji Kuramoto^a, Mingyang Gong^b, Xingbo Liu^b, Gregory Hackett^c, Kirk Gerdes^c, Teruhisa Horita^a

^a National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

^b Dept. of Mechanical & Aerospace Engineering, West Virginia University, Morgantown, USA

^c National Energy Technology Laboratory, Morgantown, USA

H I G H L I G H T S

- Stabilities of YSZ, GDC in CSG with different concentrations of PH_3 were investigated.
- Significant reactions between YSZ and GDC with 10 ppm PH_3 in CSG were confirmed.
- Reaction mechanisms between YSZ and GDC with PH_3 were clarified.
- YSZ shows better phosphorus resistance than GDC in CSG with low concentration of PH_3 .

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To clarify the chemical stability of the key materials exposed to coal syngas (CSG) containing PH_3 contaminant atmosphere, exposure tests of Y_2O_3 8 mol.% stabilized ZrO_2 (YSZ) and Gd doped CeO_2 (GDC) are carried out in simulated CSG with different concentrations of PH_3 . Significant reaction between YSZ and 10 ppm PH_3 in CSG atmosphere is confirmed, and no obvious reaction is detected on the surface of YSZ after exposed in CSG with 1 ppm PH_3 . YPO_4 , $\text{Zr}_{2.25}(\text{PO}_4)_3$ and monoclinic Y partial stabilized ZrO_2 (m-PSZ) are identified on the YSZ pellet surface after exposed in CSG with 10 ppm PH_3 . GDC reacted with PH_3 even at 1 ppm concentration. A $(\text{Ce}_{0.9}\text{Gd}_{0.1})\text{PO}_4$ layer is formed on the surface of GDC pellet after exposure in CSG with 10 ppm PH_3 . Possible reaction mechanisms between YSZ and GDC with PH_3 in CSG are clarified. Compared with GDC, YSZ exhibits sufficient phosphorus resistance for devices directly exposed to a coal syngas atmosphere containing low concentration of PH_3 .

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1. Introduction

Coal-fired power generation emits significant CO_2 and features a relatively low electrical conversion efficiency [1,2]. To reduce CO_2 and pollutant emissions and improve the thermal efficiency of coal, integrated coal gasification combined cycle (IGCC) and integrated coal gasification fuel-cell combined cycle (IGFC) systems have been developed [1–4]. An IGFC with a solid oxide fuel cell (SOFC) can directly generate and utilize coal syngas (CSG) with a high power generation efficiency [1,2]. Reliability and performance of the materials in each subsystem are the key factors for the practical IGFC applications.

CSG is a gas mixture containing H_2 , CO , CO_2 , H_2O , CH_4 , N_2 with impurities typically including H_2S , PH_3 , HCl , and AsH_3 [5]. At present, no accurate data are available that describe the nature of phosphorous compounds in the coal syngas. However, thermodynamic calculations indicate that P may exist as $(\text{P}_2\text{O}_3)_2$ (g) and PH_3 (g) in the gas cleanup system [5,6]. Hackett et al. detected very small amounts of phosphorus by ToF-SIMS and XPS in Ni-YSZ SOFC anode after cells were tested in on-line gasified coal syngas [7]. To date, no cleanup techniques can completely remove the impurities without consuming part of the syngas thermal energy [5,6]. Thus, materials with good impurities tolerance are needed for construction of the IGFC subsystems, particularly the coal gasifier, SOFC, and Gas Turbine (GT) that are directly exposed to CSG.

Stabilized zirconia doped with Y_2O_3 or Sc_2O_3 could be used in a gasifier, SOFC and GT, owing to their outstanding robustness [8–13]. In the gasifier, YSZ is utilized as a sensor material to detect

* Corresponding author. Tel.: +81 (0) 29 861 4542; fax: +81 (0) 29 861 4540.

E-mail addresses: chen-gang@aist.go.jp, chengang@smm.neu.edu.cn (G. Chen).

oxygen and carbon monoxide [8,9]. YSZ is also an excellent thermal barrier coating (TBC) material in gas turbines and jet engines to reduce the surface temperature of metallic components [10,11]. In SOFC, Yttrium or Scandium stabilized zirconia (YSZ and ScSZ) are commonly used electrolyte materials [12,13]. In addition to stabilized zirconia, the commonly used SOFC electrolyte material contains Gd- or Sm-doped ceria (SDC or GDC) and perovskite electrolyte material (strontium/magnesium doped lanthanum gallate, LSGM) [12,13].

The impurities in coal syngas with high chemical reactivity could interact with the component material of IGFC subsystem and result in serious performance degradation, particularly in SOFC [6,14–19]. Many reports have been published describing performance degradation of SOFC caused by CSG impurity poisoning [15–23]. Indeed, PH_3 contained in CSG exhibits very high reactivity with SOFC anode material even at 0.5 ppm level [15–19]. The fuel on the anode can directly flow to the electrolyte surface, thus the chemical reactivity between electrolyte materials and phosphorus in CSG has priority in the study of CSG fuelled SOFC.

Phosphorus poisoning of Ni-electrolyte cermet anodes has been reported by several authors [15–19]. Chemical reaction between Ni and phosphorus-containing fuels resulted in irreversible degradation in cell performance [16,19]. Kishimoto et al. constructed the chemical potential diagrams of Ni–P–O–H system through thermodynamic calculation to investigate the chemical stability of Ni anode in fuel containing phosphorous compounds [24]. The Ni–P–O chemical potential diagram indicated that Ni phosphide was formed at low oxygen partial pressure and high P partial pressure atmosphere, and the Ni phosphate was formed at high oxygen partial pressure and low P partial pressure atmosphere [24]. At SOFC operating condition, Ni_mP_n forms in fuel with ppb level of phosphorous [18]. Xu et al. found Ni_5P_2 and Ni_{12}P_5 as the dominant composition of Ni_mP_n in fuels with and without H_2O , respectively [16]. To date, anode material with ceramic structure is widely studied to resist phosphor poisoning [25–27]. Our recent study found that A-site deficient perovskite La-substituted SrTiO_3 (LST) could effectively suppress chemical reaction between LST and 1 ppm PH_3 in CSG better than the stoichiometric perovskite [27].

Published data indicate that cerium phosphate (CePO_4) and zirconium phosphate (ZrP_2O_7) were detected in Ni-GDC and Ni-YSZ anode material after exposure to the PH_3 -containing syngas [14–17]. However, the details of reaction mechanisms between GDC and YSZ with PH_3 in CSG are still unclear. In this study, exposure tests were carried out for pellets in CSG with different concentrations of PH_3 to clarify the reaction mechanism between YSZ and GDC with PH_3 in CSG. The chemical reactions occurring on the pellets were identified by XRD and SEM-EDS system. Possible reaction mechanisms were proposed according to characterization results.

2. Experimental

Y_2O_3 8 mol.% stabilized ZrO_2 (YSZ, Tosoh Corporation) and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (GDC, Anan Kasei Co. Ltd.) powders were pressed into pellet form by an isostatic press and sintered at 1400 °C for 5 h in air. Before exposure test, the pellet surface was polished. As-prepared YSZ and GDC discs were then placed into a high-density alumina tube for exposure testing in different CSG composition with different PH_3 concentration. The samples were raised to the testing temperature (900 °C) at a rate of 3 °C min^{-1} under a nitrogen flow. After the samples were heated overnight, the CSG was supplied to the samples. Two simulated CSG compositions were used in this study (CSG1: 17% H_2 , 39% H_2O , 16%CO and 28% CO_2 ; CSG2: 28% H_2 , 28% H_2O , 25%CO and 19% CO_2). The estimated oxygen partial pressures ($p(\text{O}_2)$) in the simulated CSG as determined from a

conventional Gibbs Free Energy minimization at 900 °C were 2.52×10^{-16} and 4.79×10^{-17} for CSG1 and CSG2, respectively. After stabilizing the tube temperature with nitrogen gas at 900 °C, simulated CSG with different concentrations of PH_3 (1 ppm and 10 ppm) were introduced into the system. The source gas cylinder was 75 ppm PH_3 with balance H_2 . Phosphine was introduced through a secondary “contaminant line”. After the samples were annealed for 100 h, the fuels were stopped and the system was set to cool down at 5 °C min^{-1} under 100% nitrogen flow. The YSZ pellets were exposed in CSG1 with 1 ppm PH_3 and CSG2 with 10 ppm PH_3 , and GDC was exposed in CSG1 with 1 ppm PH_3 and CSG1 with 10 ppm PH_3 . The phase and microstructure of pellets before and after exposure testing were examined by X-ray diffraction (XRD) and scanning electron microscope/Energy Dispersive Spectrometer + Wavelength Dispersive Spectrometer system (SEM/EDS + WDS). It should be noted that the test device (including all supply tubing) was purged by nitrogen for 8 h and the temperature was raised to 900 °C. The experiment with 1 ppm PH_3 exposure was carried out after all pipelines were replaced, to prevent cross-contamination from the higher-concentration exposure testing. This experimental protocol ensures that the specimens are exposed to the expected PH_3 concentration.

3. Results and discussion

3.1. Exposure results of YSZ

Exposure of the YSZ to 10 ppm PH_3 generated a multi-layer surface structure composed of stratified Y and Zr phases. Fig. 1 depicts the backscattered electron SEM images of the surface and the cross section of YSZ before and after exposure to different CSG and PH_3 conditions. Comparison of Fig. 1(a) (as-fabricated sample) and Fig. 1(b) (1 ppm PH_3) reveals no obvious change on the YSZ surface indicating that no obvious chemical reaction occurs between YSZ and 1 ppm PH_3 in CSG1 at 900 °C. However, as shown in Fig. 1(c), obvious changes occur on the surface of YSZ after exposure test in CSG2 with 10 ppm PH_3 . The initially smooth and dense surface of YSZ became rough after exposure as large particles formed. Fig. 1(d) shows the cross section of the YSZ pellet after exposed in CSG2 with 10 ppm PH_3 . Several layers with different colour were formed on the surface of YSZ pellet, indicating that several different phases were generated from reactions between YSZ and 10 ppm PH_3 in CSG2.

Fig. 2 shows the XRD patterns of the surface of YSZ pellets before and after exposure in different conditions. As indicated in Fig. 2(b), no obvious additional peak was observed in XRD pattern of YSZ pellet after exposed in CSG1 with 1 ppm PH_3 , which agreed well with the SEM result shown in Fig. 1(b). YPO_4 , $\text{Zr}_{2.25}(\text{PO}_4)_3$ and monoclinic Y partial stabilized ZrO_2 (m-PSZ) peaks were observed in Fig. 2(c), which confirmed that significant chemical reactions occurred on the surface of YSZ after exposed in CSG2 with 10 ppm PH_3 .

Fig. 3 shows the elemental maps of the cross section of the YSZ pellet after exposure test in CSG2 with 10 ppm PH_3 . Here the maps of P, Y and Zr were identified by WDS due to the adjacent peaks of P, Y and Zr in EDS pattern. As indicated in the elemental map shown in Fig. 3, the main constituents of the light grey surface phase are Y and P, and the main constituents of the dark grey phase are Zr and P. Highlighted P can be observed in both layers (light grey layer and dark grey layer). The Y map exhibits a thin Y-enriched layer under the dark grey phase layer. Under the Y enriched layer, a layer exists with insufficient Y and enriched Zr, with limited P also observed.

Table 1 shows the point analyses of the additional phase layers apparent in the SEM cross section image of Fig. 3. The detection area of EDX “point” analysis is actually a circular region approximately 1 μm in diameter. Therefore, the data in Table 1 are used as a

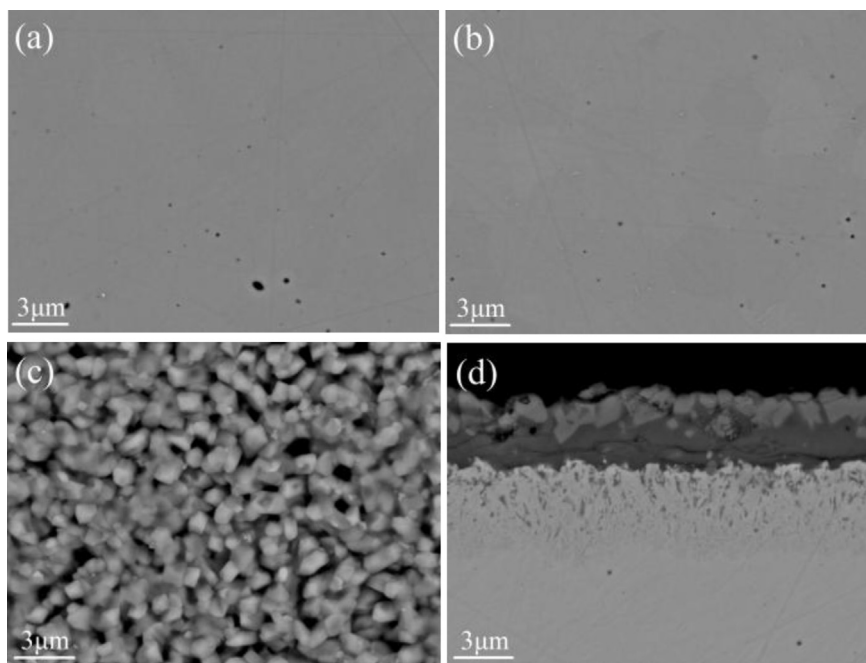


Fig. 1. SEM images of the surface and the cross section of YSZ pellets before and after exposure in different conditions, (a) surface of fresh pellet, (b) surface after exposure to CSG1 with 1 ppm PH_3 , (c) surface after exposure to CSG2 with 10 ppm PH_3 , (d) cross section after exposure to CSG2 with 10 ppm PH_3 .

qualitative reference to support the XRD and SEM/WDS results. According to atomic ratio of each element and the XRD result shown in Fig. 2(c), the main phase of the light grey layer (spectrum 1, 2 and 3) is YPO_4 , and the dark grey phase is $\text{Zr}_{2.25}(\text{PO}_4)_3$ (spectrum 4, 5 and 6). The main phases around spectrum 7, 8 and 9 could be m-PSZ and little YPO_4 . The YPO_4 phase under the dark grey layer is scattered near the $\text{Zr}_{2.25}(\text{PO}_4)_3$ layer, under which is the m-PSZ layer. Under the m-PSZ layer is the YSZ without reaction. The thickness of the reaction layer (including YPO_4 , $\text{Zr}_{2.25}(\text{PO}_4)_3$ and m-PSZ layers) in the YSZ pellet shown in SEM image of Fig. 3 is about 10 μm .

3.2. Exposure results of GDC

Fig. 4 shows the backscattered electron SEM images of the GDC pellet surface before and after exposure in CSG1 with different PH_3

concentrations at 900 °C for 100 h. As indicated in Fig. 4 (a), (b) and (c), obvious structural and morphological changes were observed on the surface of GDC pellets after exposure test in CSG1 with 1 ppm and 10 ppm PH_3 . The appearance of the GDC surface depended on the PH_3 exposure condition. Compared with the smooth surface of the fresh GDC pellet, the GDC pellet surface became rough after exposure in CSG1 with 1 ppm PH_3 (as shown in Fig. 4 (b)), but the GDC pellet surface remained smooth after exposure in CSG1 with 10 ppm PH_3 (as shown in Fig. 4 (c)). Big particles and clear grain boundaries between each particle were observed.

The backscattered electron SEM image shown in Fig. 4(d) indicates that an additional 3 μm thick phase layer (different extrinsic feature compared with GDC phase) was formed on the surface of GDC pellet after exposed in CSG1 with 10 ppm PH_3 . Moreover, compared with the GDC pellet, the mechanical strength of the additional phase layer is very low, and the connectivity between the generated phase layer and GDC is also poor. Thus, the additional phase layer formed on the GDC surface can be easily crushed and peeled.

Fig. 5 shows the XRD patterns of the GDC pellet surface before and after exposure in CSG1. Additional phase peaks were observed in each sample after exposure in CSG1 with 1 ppm PH_3 and in CSG1 with 10 ppm PH_3 , respectively. According to the intensities of additional phase depicted in Fig. 5 (b) and (c), more significant reactions occurred on the surface of GDC exposed in CSG1 with 10 ppm PH_3 . The additional phase peaks in XRD pattern essentially correspond with monazite $\text{Ce}(\text{PO}_4)$ [28]. No obvious peak in the pattern matched any known Gd phosphate.

Fig. 6 depicts the elemental maps of the GDC pellet cross section after exposure testing in CSG1 with 10 ppm PH_3 . From Fig. 6, the main constituents of the additionally formed surface phase are Ce, Gd and P. Table 2 shows the lattice parameters of the additional phase shown in the XRD pattern of Fig. 5(c), which are monazite CePO_4 and GdPO_4 reported in Refs. [28–30]. The structure of monazite is generally described as the nine-fold coordination of the metallic cation interpenetrated by a tetrahedron constructed from 4 oxygen atoms belonging to two bidentate tetrahedrons [30]. As indicated in the XRD pattern of Fig. 5(c), the peak positions of the

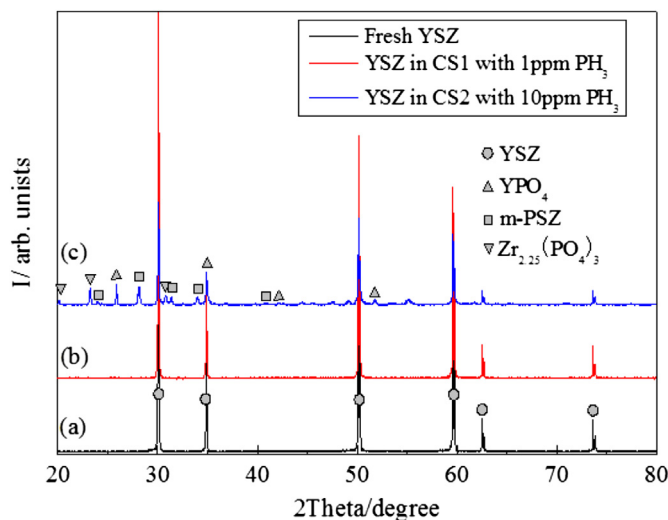


Fig. 2. XRD patterns of the surface of YSZ pellets before and after exposure to different conditions, (a) fresh pellet, (b) in CSG1 with 1 ppm PH_3 , (c) in CSG2 with 10 ppm PH_3 .

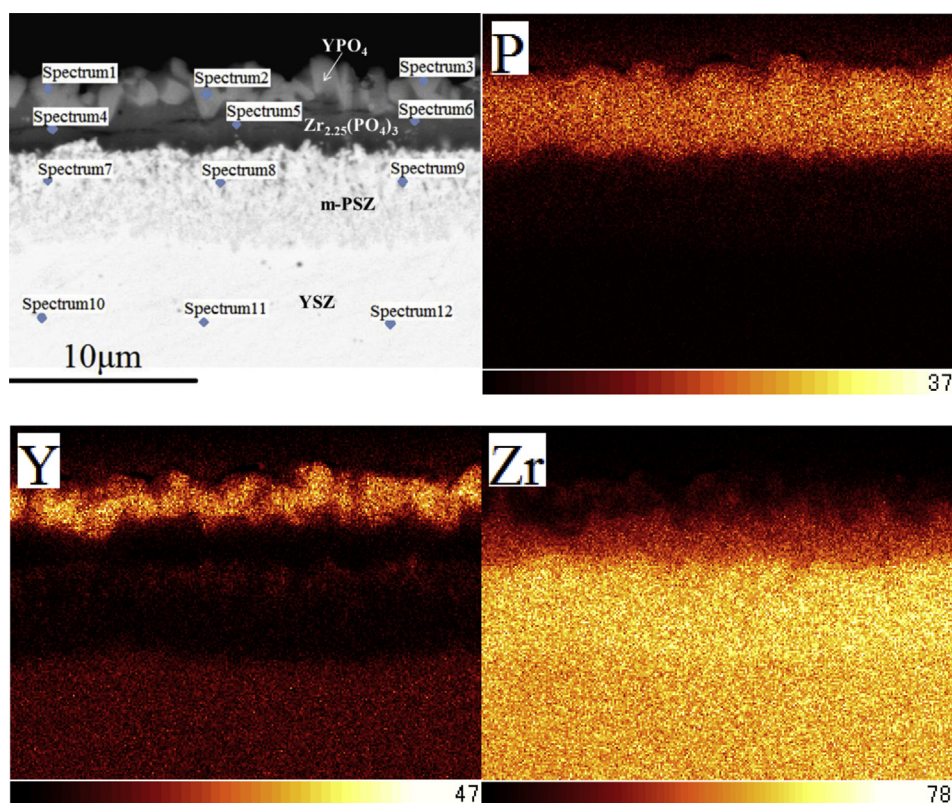


Fig. 3. Elemental maps of the cross section of YSZ pellet after exposure testing in CSG2 with 10 ppm PH_3 .

Table 1
Point analysis of the additional phase layer indicated in cross section SEM image of Fig. 3.

Spectrum no.	Elemental (at.%)				Possible phase compositions
	O	Y	Zr	P	
Spectrum 1	67.2	13.5	2.0	17.2	YPO ₄ + Zr _{2.25} (PO ₄) ₃
Spectrum 2	67.4	13.9	1.5	17.2	
Spectrum 3	65.9	15.0	1.3	17.8	
Spectrum 4	69.8	0	13.5	17.6	Zr _{2.25} (PO ₄) ₃
Spectrum 5	70.7	0	13.9	16.6	
Spectrum 6	71.5	0	13.4	16.0	
Spectrum 7	69.0	1.2	29.5	0.3	m-PSZ + YPO ₄
Spectrum 8	68.5	3.0	26.3	2.2	
Spectrum 9	67.3	3.3	26.6	2.8	
Spectrum 10	67.3	4.9	29.9	0	YSZ
Spectrum 11	67.7	4.5	29.0	0	
Spectrum 12	67.0	4.7	29.5	0	

additional phase principally agree with those of CePO_4 . Thus, the lattice parameters of the additional phase were calculated with the indices of CePO_4 . The atomic radius of Ce and Gd were 1.85 Å and 1.8 Å, respectively [30]. The average bond distances of Ce–O (2.556 Å) in the ninefold coordination geometry of CePO_4 were smaller than those of Gd–O (2.469 Å) in the ninefold coordination geometry of GdPO_4 . The bond distances of P–O in tetrahedrons of CePO_4 and GdPO_4 were 1.538 Å and 1.53 Å, respectively [28,29]. From Table 2, all of the parameters (a, b, c and β) of additional phase were slightly diminished compared to CePO_4 but larger than GdPO_4 . The diminished lattice parameters (compared with CePO_4) indicate that the additional phase is not pure monazite CePO_4 , but may be an incorporated phosphate monazite $(\text{CeGd})\text{PO}_4$.

Table 3 shows the point analysis of the additional phase layer indicated in the SEM image of Fig. 6. The point analyses shown in Table 3 were also used as reference due to the detection limitation of EDX measurement. Based on the lattice parameter indicated in Table 2 and the XRD results shown in Fig. 5, the main phase of Spectrum 1, 2 and 3 is $(\text{Ce}_{0.9}\text{Gd}_{0.1})\text{PO}_4$, and the main phase of Spectrum 4–9 was GDC. The atomic ratio of Gd: Ce in Spectra 1–9 in Table 3 show small deviations from the theoretical value of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$, which is attributable to the measurement error of EDX device.

4. Discussion

4.1. Reaction mechanism of YSZ

In present case, the $p(\text{O}_2)$ of CSG was mainly dominated by $\text{H}_2/\text{H}_2\text{O}$ equilibrium due to the slow equilibrium reaction of CO/CO_2 . Ellingham diagram for the P–H–O system has been reported by Kishimoto et al. [24]. At 900 °C, PH_3 was easily oxidized in P_2O_5 in

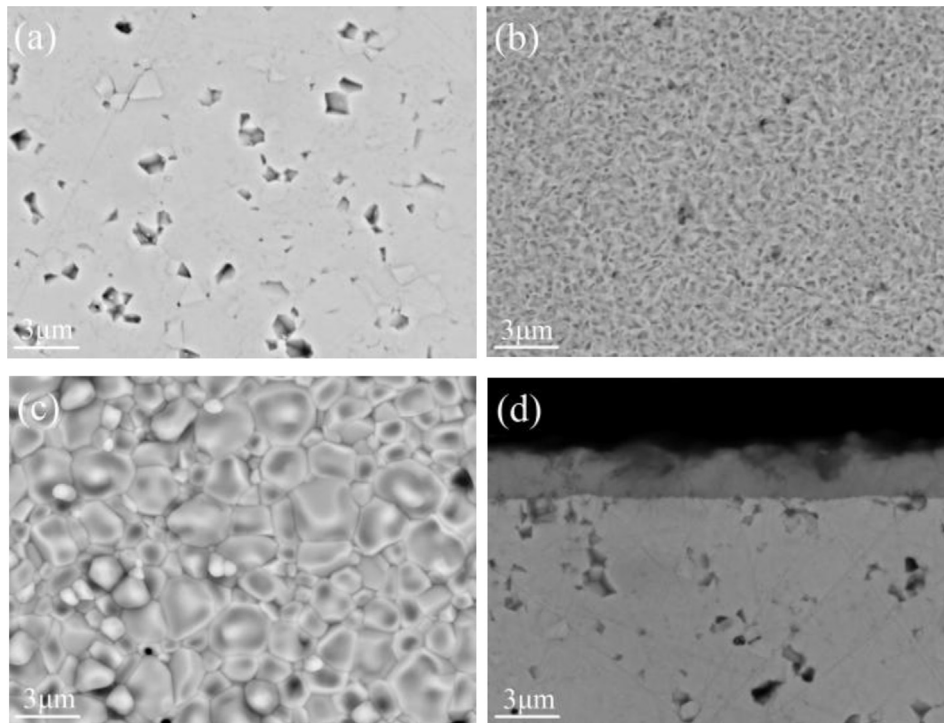
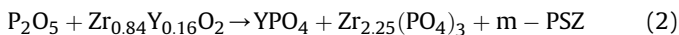


Fig. 4. SEM images of the surface and the cross section of GDC pellets before and after exposure to different conditions, (a) surface of fresh pellet, (b) surface after exposure to CSG1 with 1 ppm PH_3 , (c) surface after exposure to CSG1 with 10 ppm PH_3 , (d) cross section after exposure to CSG1 with 10 ppm PH_3 .

the region with relative high oxygen potential. Aggregate results for YSZ indicate that the main reaction between YSZ and 10 ppm PH_3 can be expressed as:



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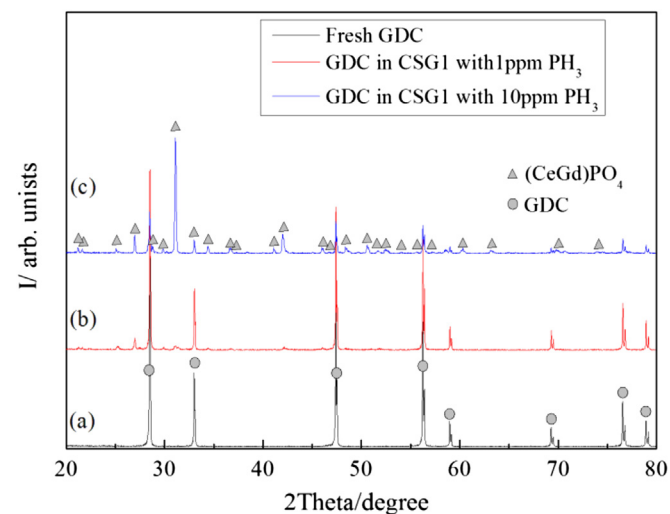
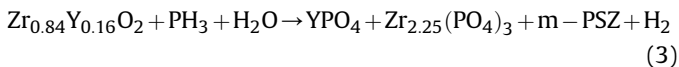
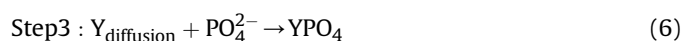
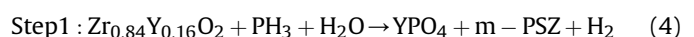


Fig. 5. XRD patterns of the surface of GDC pellets before after exposure to CSG1 with different PH_3 concentrations, (a) fresh pellet, (b) in CSG1 with 1 ppm PH_3 , (b) in CSG1 with 10 ppm PH_3 .

The YPO_4 layer generated on the surface of YSZ (as depicted in Fig. 3) indicates that formation depends on diffusion of bulk Y to the YSZ surface. Formation of m-PSZ indicates that the Y reaction with PH_3 is more active, and the stability of YPO_4 is better than that of $\text{Zr}_{2.25}(\text{PO}_4)_3$. Phase transformation (from cubic to monoclinic) in YSZ results from decreasing the Y_2O_3 concentration [31–33]. In this case, quantification of the Y concentration in m-PSZ is not possible since it may be very low and transitional. As depicted in Fig. 3 and reported in Table 1, four stratified layers were formed owing to chemical reactions and elemental diffusion. From surface to interior the layers are: YPO_4 , $\text{Zr}_{2.25}(\text{PO}_4)_3$, m-PSZ plus minor YPO_4 , and YSZ layer, respectively. From these, we can deduce that several conditions are required to form the heterophase multi-layers: (1) Y reacts with low concentrations of phosphorus; (2) Zr only reacts with relatively high concentrations of phosphorus; (3) Y could diffuse into m-PSZ and YSZ; (4) Y cannot diffuse into $\text{Zr}_{2.25}(\text{PO}_4)_3$.

To better understand how the reactions occurred on YSZ pellet with 10 ppm PH_3 exposure, a possible reaction schematic is depicted in Fig. 7. Three sequential steps are postulated.

In step 1, PH_3 in CSG firstly reacts with Y on the surface of YSZ and forms the YPO_4 due to relatively high reactivity of Y in YSZ. Meanwhile, segregation of Y in YSZ results in formation of m-PSZ in place. In step 2, the Zr in m-PSZ possesses relatively higher chemical potential than in 8 mol%-YSZ and reacts with PH_3 and H_2O to form $\text{Zr}_{2.25}(\text{PO}_4)_3$. More YPO_4 and m-PSZ form on the surface and interior of YSZ in step 2 owing to bulk diffusion of Y to the pellet surface. Y existing in the m-PSZ layer and in YPO_4 near the m-PSZ layer rapidly reacted or diffused in this step.



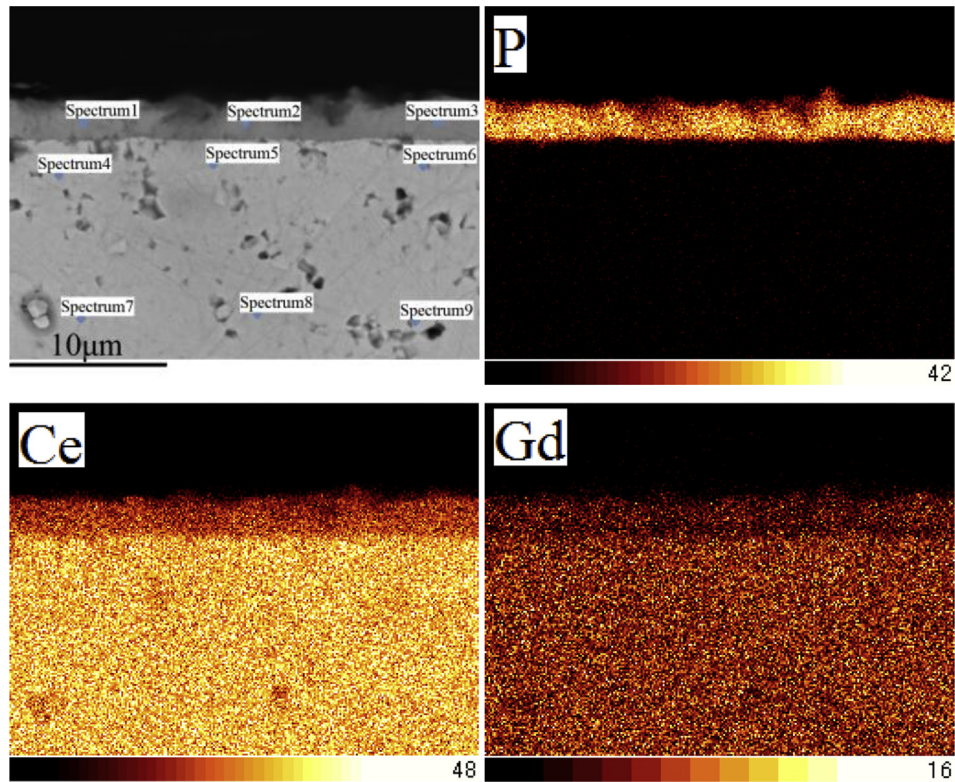
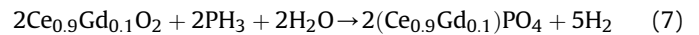


Fig. 6. Elemental maps of the cross section of GDC pellet after exposure testing in CSG1 with 10 ppm PH_3 .

The scattered $\text{Zr}_{2.25}(\text{PO}_4)_3$ nucleated and grew with annealing time in step 2, eventually coalescing to form a dense layer in step 3. From point analysis result of Y shown in Table 1 and the Y map shown in Fig. 3, no Y exists in $\text{Zr}_{2.25}(\text{PO}_4)_3$ layer, which indicates that Y does not diffuse into the $\text{Zr}_{2.25}(\text{PO}_4)_3$ layer. In other words, no more YPO_4 was formed on the surface of YSZ after the dense $\text{Zr}_{2.25}(\text{PO}_4)_3$ layer formed under the surface YPO_4 layer. Scattered YPO_4 formed under dense $\text{Zr}_{2.25}(\text{PO}_4)_3$ layer shown in Fig. 3 indicates that the activity of P in m-PSZ is sufficient to form YPO_4 (as indicated in Eq. (6)), but insufficient to form $\text{Zr}_{2.25}(\text{PO}_4)_3$. Here, to form such scattered YPO_4 , Y should diffuse from inside of m-PSZ or YSZ until the chemical potential of P diminishes to the minimum value for Y reaction. In this study, no obvious chemical reactions occurred on the surface of YSZ after exposure to CSG1 with 1 ppm PH_3 , indicating that the reactivity of Y and Zr in YSZ may be insufficient to react with 1 ppm PH_3 in CSG1. The zirconia electrolytes are potentially compatible electrolytes for CSG containing 1 ppm level PH_3 in SOFC.

4.2. Reaction mechanism of GDC

Data presented in Fig. 6 and Table 3 for the GDC pellet indicate that a $(\text{Ce}_{0.9}\text{Gd}_{0.1})\text{PO}_4$ layer formed on the surface after exposure to CSG1 with 10 ppm PH_3 . A possible reaction is expressed as:



Clavier et al. summarized that the natural monazites generally can incorporate lanthanides from lanthanum to lutetium with various chemical compositions, and La and Ce are identified as predominant in most cases [30]. The formation of homogeneously incorporated monazites with solid state reaction method requires stringent conditions in temperature, elements, and atmosphere [30,34]. The separation of YPO_4 and $\text{Zr}_{2.25}(\text{PO}_4)_3$ in YSZ sample in this study also indicates that the formation of incorporated monazites requires specific conditions. In this case the formation of $(\text{Ce}_{0.9}\text{Gd}_{0.1})\text{PO}_4$ indicates that Ce and Gd might have similar

Table 3

Point analysis of the additional phase layer indicated in cross section SEM image of Fig. 6.

Spectrum no.	Elemental (at.%)				Possible phase compositions
	O	Ce	Gd	P	
Spectrum 1	63.5	15.8	1.7	19.0	$(\text{Ce}_{0.9}\text{Gd}_{0.1})\text{PO}_4$
Spectrum 2	60.4	17.1	2.1	20.4	
Spectrum 3	63.9	15.4	1.8	18.9	
Spectrum 4	66.0	30.5	3.4	0	GDC
Spectrum 5	67.0	30.0	2.9	0.1	
Spectrum 6	66.6	29.8	3.4	0.2	
Spectrum 7	68.1	29.2	2.8	0	
Spectrum 8	67.9	28.7	3.4	0	
Spectrum 9	67.3	29.1	3.5	0	

Table 2

Lattice parameter of additional phase formed on the surface of GDC.

Materials	Lattice parameters						
	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)
(CeGd) PO_4	6.779	7.014	6.454	90°	103.19°	90°	298.77
CePO_4 [19]	6.788	7.016	6.465	90°	103.43°	90°	299.92
GdPO_4 [20]	6.621	6.823	6.31	90°	104.16°	90°	276.6

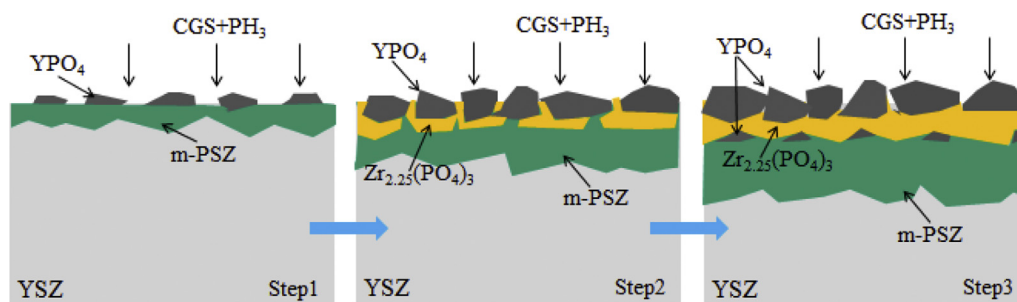


Fig. 7. Postulated reaction schematic between YSZ and 10 ppm PH_3 in CGS.

chemical reaction potentials with PH_3 in the CSG atmosphere, therefore Ce and Gd might react simultaneously with PH_3 . Exposure test results of GDC indicate that the reactivity of 1 ppm PH_3 is sufficient for both Ce and Gd. Future use of GDC in a coal syngas fuelled cell requires examination of GDC reactivity with PH_3 at much lower PH_3 concentrations.

5. Conclusions

The chemical potential of 10 ppm PH_3 in coal syngas is sufficient to react with YSZ. YSZ showed good phosphorus resistance at 1 ppm PH_3 exposure in CSG. Segregation and diffusion of yttrium in YSZ are the dominant processes for chemical reactions between YSZ and PH_3 in CGS with 10 ppm PH_3 . Stratified YPO_4 , $\text{Zr}_{2.25}(\text{PO}_4)_3$ and monoclinic Y partial stabilized ZrO_2 formed sequentially from the surface to interior of the YSZ after exposure to CSG2 with 10 ppm PH_3 . $(\text{Ce}_{0.9}\text{Gd}_{0.1})\text{PO}_4$ was formed on the surface of both GDC pellets after exposure to CSG with 1 ppm PH_3 and with 10 ppm PH_3 , indicating that GDC is more susceptible to degradation in CSG containing 1 ppm PH_3 than YSZ.

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